

SCIENCE FOR GLASS PRODUCTION

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THE EFFECT OF TITANIUM DIOXIDE ON STRUCTURE AND PROPERTIES OF BORON-FREE GLASSES

Ya. I. Belyi¹ and N. A. Minakova¹

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IR spectroscopic and x-ray phase analysis established the structural specifics of glasses in the system $\text{Na}_2\text{O} - \text{SiO}_2 - \text{TiO}_2 - \text{Na}_3\text{AlF}_6$, as well as the dependence on the type of crystallizing phases on the chemical composition of the glass matrix. The effect of the structure of titanium-bearing clusters on the leachability of glasses, the effect of the second coordination sphere on the coordination of the central cation (Ti^{4+}), and the propensity of experimental glass coatings to opacification are registered.

The expanding areas of industrial application of titanium-bearing glasses necessitate a further improvement of their technological parameters and service characteristics by developing a required structure, which to a great extent depends on their chemical compositions. This is corroborated, for instance, by the fact that the only enamels widely used in producing household ware are boron-bearing titanium enamels, since boric anhydride contained in them makes it possible to decrease their alkali oxide content and thus to decrease the opacity of coatings. Boron-free enamels are not found in enameling practice, since the effect of their chemical composition on glass structure and the formation of titanium-bearing phases under additional heat treatment is not sufficiently known. Considering that boron-bearing materials are scarce and expensive and boric anhydride, which is leached from enamel coatings, is toxic, research on the structure and properties of boron-free titanium-bearing glasses appears topical.

Many authors relate the crystallization of TiO_2 in glasses under repeated thermal treatment to the hexahedral coordination of titanium ions and the position of the modifiers in their structural lattice. Glasses in which four-coordination Ti^{4+} takes the position of the lattice-forming agent remain non-opacified.

The presence of titanium ions of a certain coordination in glasses is usually identified based on their IR spectra. Particular coordinations of titanium ions in glasses correspond to absorption bands of different frequencies; for instance,

$[\text{TiO}_6]$ is related to $500 - 600$ or $500 - 700 \text{ cm}^{-1}$ [1, 2] and $[\text{TiO}_4]$ is related to $700 - 960 \text{ cm}^{-1}$; the latter range is attributed to titanium in five-coordination as well [2].

Some authors have commented [2, 3] on the difficulty of identifying the coordination state of the titanium ion and the incorrectness of interpreting titanium-bearing glass spectra by comparing them to the respective spectra of crystalline compounds, since even the latter structures that have specific linking of titanium polyhedrons exhibit significant variations in the wave numbers of characteristic bands for the same coordination of Ti^{4+} [2]. This may be attributed to the effect of so-called second coordination sphere understood as the set of ions linked to the (central) cation considered via oxygen atoms (Fig. 1). In our opinion, it is the second coordination sphere that determines the oxygen environment of the central cation Ti^{4+} in silicate glasses.

The authors have performed the spectroscopic study of glasses in the range of $\text{Na}_2\text{O} - \text{SiO}_2 - \text{TiO}_2 - \text{Na}_3\text{AlF}_6$ sys-

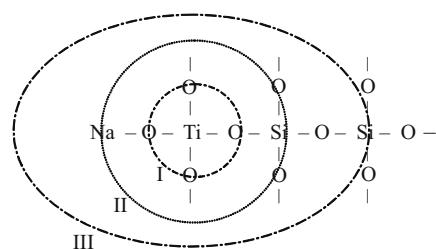


Fig. 1. Scheme of coordination spheres of titanium ion in silicate glass: I, II, and III) the first, second, and third coordination spheres.

¹ Ukrainian State Chemical Engineering University, Dnepropetrovsk, Ukraine.

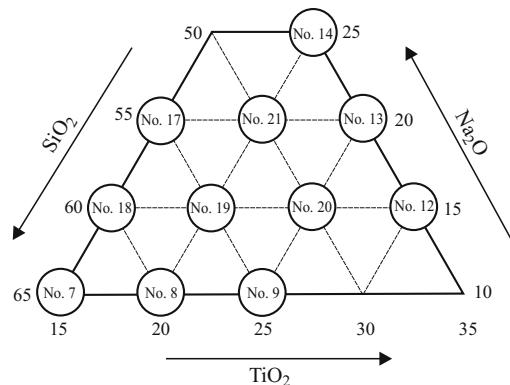
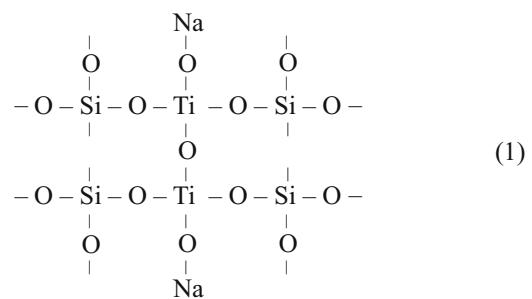


Fig. 2. Range of investigated glasses in $\text{Na}_2\text{O} - \text{SiO}_2 - \text{TiO}_2 - 10\text{Na}_3\text{AlF}_6$ system.

tem indicated in Fig. 2 for comparative analysis and identification of structural transformations and specifics of crystallizing glasses depending on their compositions. It is interesting to study the way the IR spectra data correlate with other properties of glasses in the specified system range. Absorption spectra (Fig. 3) were recorded with a Spekord-M80 spectrophotometer (K. Zeiss) in the frequency range of $1700 - 400 \text{ cm}^{-1}$.

The obtained spectra have three wide absorption bands in the range of $1350 - 850$, $850 - 700$, and $550 - 400 \text{ cm}^{-1}$. The band at $1350 - 850 \text{ cm}^{-1}$ in glass No. 7 (Figs. 2 and 3)

has the main maximum at 1100 cm^{-1} and a weaker maximum at 1200 cm^{-1} . This indicates that the structural lattice of this glass consists of several different types of polyhedrons. The band at 1100 cm^{-1} is related to stretching $\text{Si} - \text{O} - \text{Si}$ vibrations of skeleton silicon-oxygen groups in the 3D glass lattice. The shift of its maximum to the low-frequency range (1050 cm^{-1}) when SiO_2 is replaced by TiO_2 (glass No. 8) may be caused, on the one hand, by a decreased degree of link covalence in $[\text{SiO}_{4/2}]^{4-}$ anions when titanium polyhedrons are incorporated into the silicon-oxygen glass skeleton and on the other hand, by the growing intensity of the absorption band of five-coordination Ti^{4+} , namely, the emerging valence link $\text{Ti} - \text{O} - \text{Ti}$ in the following groups:



The above is corroborated by the increased crystallization capacity, for instance, in glass No. 8, which is registered by the x-ray phase analysis of enamel coatings. The absorption band at 1200 cm^{-1} in this glass is presumably related to

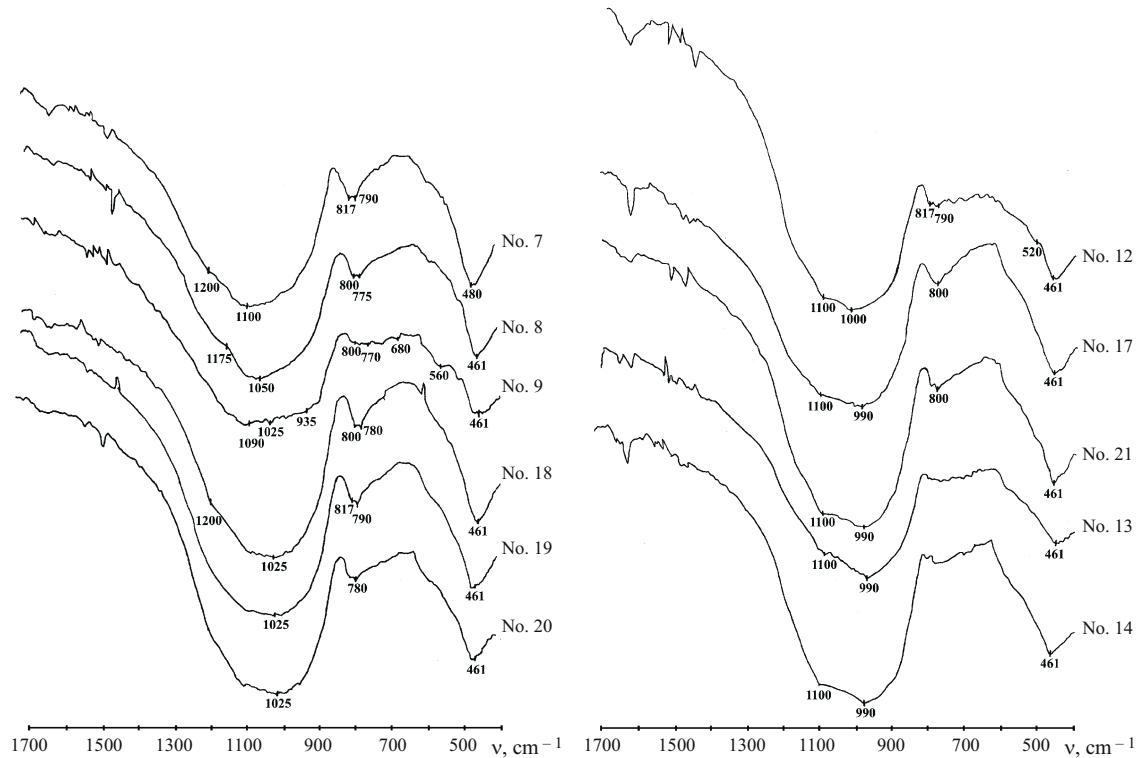
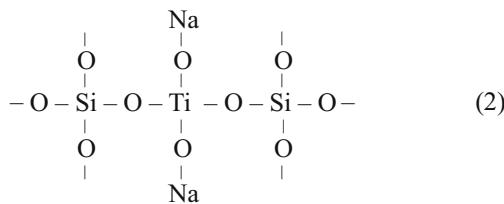


Fig. 3. IR absorption spectra of experimental glasses.

possible stretching vibrations of four-coordination titanium, namely, to $\text{Ti} - \text{O} - \text{Si}$ links of the following groups:

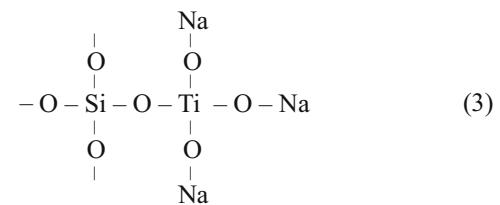


As the content of TiO_2 grows from 15 to 20% (here and elsewhere weight content unless otherwise specified), this band shifts to the low-frequency range (1175 cm^{-1}) and completely disappears upon reaching the molar ratio of $\text{Na}_2\text{O} : \text{TiO}_2 = 0.5$ in glass No. 9. This is caused by the weakening of the $\text{Ti} - \text{O} - \text{Si}$ link under an insufficient amount of alkali oxides, which contributes to strengthening the $\text{Ti} - \text{O}$ link, and the transition of titanium ions from the four-coordination to the five-coordination state. At the same time, the water resistance of frit drops from $0.032 \text{ cm}^3/\text{g}$ (glass No. 7) to $0.055 \text{ cm}^3/\text{g}$ (glass No. 8).

The structural lattice of glass No. 9 containing 25% TiO_2 is heterogeneous, since it has several absorption bands in the same range (cm^{-1}): $1090 [\text{SiO}_4]^{4-}$, $1025 [\text{TiO}_5]^{4-}$, and $935 [\text{TiO}_6]^{4-}$. This is confirmed by the fact that this glass crystallizes even under fast chilling of its melt (fritting into water), as a consequence of which the absorption band typical of the crystalline phases of anatase and rutile emerges at 560 cm^{-1} as well. The absorption band with the maximum at 480 cm^{-1} (glass No. 7) can be attributed to the deformation vibrations of the silicon-oxygen groups. As the TiO_2 content increases to 25% (glass No. 9), this maximum shifts to the short-wave range of 461 cm^{-1} (glass No. 7) and becomes weaker. The absorption in the range of $850 - 700 \text{ cm}^{-1}$ with maxima at 817 and 790 cm^{-1} (glass No. 7), as the quantity of TiO_2 grows to 20% (glass No. 8), shifts toward lower wave numbers (800 and 775 cm^{-1}), which may be caused by the vibrations of the $\text{Ti} - \text{O} - \text{Na}$ link in groups (2), whose quantity decreases as well with an increasing TiO_2 content. The absence of a clearly expressed absorption maximum in the range of $850 - 700 \text{ cm}^{-1}$ in glass No. 9 (Fig. 3) and the bands in the range of 1200 cm^{-1} are related to the disappearance of four-coordination titanium, i.e., the disappearance of groups (2). The increased water resistance of this glass, in our opinion, is due to the liquation phenomena in them and the separation of the alkali-titanate components in the form of a droplet phase, which leads to the glass depletion of alkali oxides and, consequently, the water resistance of this frit growing to $0.0116 \text{ cm}^3/\text{g}$.

In more alkaline glasses (Nos. 12, 18 – 20) the total form of absorption curves (Fig. 3) virtually does not change; however, as the content of Na_2O grows to 15%, the absorption band at $1350 - 850 \text{ cm}^{-1}$ with a maximum of 1100 cm^{-1} (glass No. 7) is slightly shifted to the low-frequency range with the maximum at 1025 cm^{-1} , which is related to the

depolymerization of the silicon-oxygen glass lattice raising the leachability of the frit from $0.032 \text{ cm}^3/\text{g}$ (glass No. 7) to $0.180 \text{ cm}^3/\text{g}$ (glass No. 18). The shift in the absorption band in the frequency range of $820 - 650 \text{ cm}^{-1}$ from 817 and 790 cm^{-1} in low-alkali glasses (Nos. 7 and 8) to 800 and 780 cm^{-1} , as the quantity of Na_2O grows (glass No. 18), may be caused by the weakening of the $\text{Ti} - \text{O} - \text{Na}$ bond in the groups:



and its increased strength in glass (No. 19) with the molar ratio of $\text{Na}_2\text{O} : \text{TiO}_2 \approx 1$. Furthermore, glass No. 19 has virtually no boundary between the two absorption bands for the tetrahedrons $[\text{SiO}_{4/2}]^{4-}$ and $[\text{TiO}_{4/2}]^{4-}$, which points to a sufficiently high homogeneity of glass and is corroborated by its water resistance growing to $0.085 \text{ cm}^3/\text{g}$ compared to glass frit No. 18 ($0.180 \text{ cm}^3/\text{g}$).

An increase in the quantity of TiO_2 to 25% (Fig. 3, glass No. 20) narrows the main absorption band ($1300 - 850 \text{ cm}^{-1}$) by shifting its high-frequency limit to the low-frequency range, which may be caused by the decreasing amount of four-coordination titanium. At the same time, the absorption at the range of $750 - 625 \text{ cm}^{-1}$ intensifies due to the growth in the number of $\text{Ti} - \text{O} - \text{Na}$ links in groups (1), which raises the leachability of glasses (No. 20) to $0.26 \text{ cm}^3/\text{g}$.

The absorption band in the range of $550 - 400 \text{ cm}^{-1}$ with and increasing TiO_2 content becomes differentiated as a consequence of the formation of links with various groups of titanium-oxygen complexes emerging in the glass structure, which have different deformation effects on its polyhedrons. Thus, glass No. 12 has an absorption maximum at 520 cm^{-1} caused by the six-coordination titanium (in the condensed state) [4, 5], which is formed as a result of the polymerization of its polyhedrons. The alkali-titanate component is separated as an individual phase due to the incompatibility of the TiO_2 and Na_2O structural complexes in a highly viscous silicate glass. As a result of the secondary heat treatment, the high-titanium phase expands by merging individual sites with identical compositions, which leads to the intense crystallization of glass. Liquation phenomena having a positive effect on the opacity of glass coatings Nos. 12 and 9 are clearly registered in their dilatometric expansion curves (Fig. 4). In the expansion curves of other experimental glasses (including glass No. 14 with rather high TiO_2 content) liquation is not identified.

The increase in the quantity of Na_2O in glasses Nos. 13, 17, and 21 to 20% and in glass No. 14 to 25% (Figs. 2 and 3) produces a more substantial shift of the main absorption maximum (1100 cm^{-1}) to the low-frequency range ($990 -$

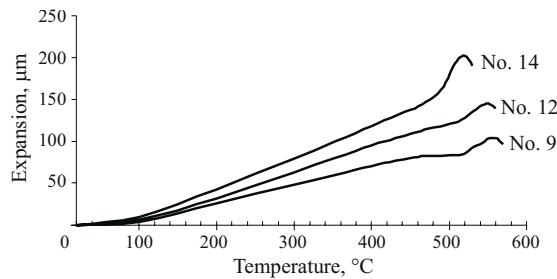


Fig. 4. Expansion of experimental glasses depending on temperature.

980 cm^{-1}). This is related to the intensified polymerization of the structural lattice of the specified glasses, which is corroborated by the increased leachability of their frits to $0.24 - 0.39\text{ cm}^3/\text{g}$.

In glasses Nos. 13 and 14, in which the molar content of SiO_2 is about 50%, the absorption band in the range of $750 - 825\text{ cm}^{-1}$ is virtually absent, which may be caused by significantly weakening of the polarizing effect of silicon ions on titanium polyhedrons, as the bond between the silicon ions is implemented only on the interface between the siliceous and the alkali-titanate glass. This is confirmed by x-ray phase analysis of the glass coatings, in which the crystalline phase is $\text{Na}_2\text{O} \cdot 6\text{TiO}_2$ [6] and not alkaline titanium-silicates, as reported in [7, 8].

Thus, TiO_2 in alkali-silicate glasses is most frequently found in the form of clusters (1) – (3); furthermore, TiO_2 in cluster (2) has three absorption bands: in the range of 1200 cm^{-1} for the $\text{Ti} - \text{O} - \text{Si}$ link, 800 cm^{-1} for the $\text{Ti} - \text{O} - \text{Na}$ link, and in the frequency range below 500 cm^{-1} the deformation vibration band. The absorption band of the $\text{Ti} - \text{O} - \text{Si}$ link in cluster (1) does not undergo substantial changes and the band typical of the $\text{Ti} - \text{O} - \text{Na}$

link shifts to the low-frequency range, as a consequence of decreased strength due to a strong polarizing effect of the silicon ions. The decreasing strength of $\text{Ti} - \text{O} - \text{Si}$ and $\text{Ti} - \text{O} - \text{Na}$ links in cluster (3), which has an additional absorption band in the range of $900 - 1000\text{ cm}^{-1}$, produces a shift of their characteristics bands to 1100 and 750 cm^{-1} , respectively.

All this confirms our hypothesis on the significant effect of the second coordination sphere on the coordination of the main cation (Ti^{4+}) and the wave numbers of characteristic bands. The third coordination sphere in this case also has a slight effect on various shifts of absorption bands in silicate glasses.

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